# ANALYSIS OF CURING CYCLE EFFECT ON PROCESSING VOIDS DISTRIBUTION AND MECHANICAL PROPERTIES OF A POLYMER COMPOSITE MATERIAL

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## Abstract
*AS4/8552 Unidirectional and multiaxial composite material manufactured by compression moulding is analyzed through X-ray computer tomography experiments. Three a priori temperature cycles were designed based on the rheological and thermal behavior of raw prepreg material. The void distribution, in terms of volume fraction size, and geometry, was analyzed using the three dimensional X-ray tomography of the composite samples extracted from the composite panels. The tomograms revealed a clustered dispersion of elongated voids well aligned with the fiber orientations which were not uniformly distributed along the width and thickness of the samples. The larger voids exhibited a rod-like shape while smaller tended to spheres. Additionally, mechanical tests were performed on specimens machined from the composite panels manufactured (interlaminar shear strength (ILSS), interlaminar fracture toughness ($G_{Ic}$ and $G_{IIc}$), in-plane compression strength, drop-weight impact and compressive residual strength (CAI)) in order to ascertain the effect of the processing voids on the mechanical performance of the composite material.*

## 1 Introduction
Fiber-reinforced polymer-matrix composites are nowadays extensively used in structural elements due to their high specific stiffness and strength. For high-performance components, manufacturing is carried out using prepreg laminas, which are stacked (either manually or with an automatic lay-up machine) and consolidated under the simultaneous application of pressure and temperature in an autoclave. Autoclave pressure impedes the growth of voids or even leads to the collapse of air bubbles, giving rise to materials with excellent mechanical properties and very low porosity, as required by aerospace and sports industries. However, this manufacturing route is expensive in terms of capital investment and processing time and it is not cost-effective for use in other industrial sectors. These limitations had acted as driving forces to look for alternative out-of-autoclave processing routes.

The increasing demand of innovative prepregs systems suitable for out-of-autoclave techniques has required to achieve a considerable control on all the aspects related to the manufacturing process in order to obtain composite parts maintaining the quality with reduced environmental footprint (e.g. same qualified resin transfer moulding, SQRTM, QuickStep, etc.). Generally speaking, those processing techniques alternative to the well established autoclave tradition tend to produce materials with a lower mechanical performance due to voids and porous grown during the process. The pressure magnitude, the application time during within the cure cycle, and the resin viscosity evolution due to change in the temperature have a crucial effect on the void content of laminates [1,2]. A number of previous works have revealed the detrimental effect of the porosity on the mechanical performance of polymeric composite materials [3].

## 2 Material

The prepreg used in the current studies was a commercial unidirectional tape of carbon fiber and epoxy matrix HexPly AS4/8552 supplied by Hexcel Co.. The epoxy matrix system is HexPly-8552 consisting of a mix of a high functionality epoxy resin, Tetraglycidyl methylenedianiline (TGMDA) (15-40%w), and a lower functionality epoxy resin, Triglycidyl *p*-aminophenol (TGpAP) (15-40%w), modified with thermoplastic particles, the curing agents are: 4,4’diaminodiphenylsulfone (DDS) (10-30%w) and 3,3’diaminodiphenylsulfone (1-15%w). The reinforcement is a polyacrylonitrile-based high strength carbon fiber, AS4. The nominal resin content of the prepreg is 34%w and the nominal areal weight is 194g/m$^2$.

## 3 Definition of cure cycles

Three cure cycles -named C-1, C-2 and C-3- were used to manufacture composite panels with different levels of porosity. These cycles have been especially designed by using rheological and thermal measurements criteria in order to optimize the porosity level when using the compression moulding processing route. The processing window, as the interval time with minimum values of the viscosity of the resin, was measured and used to establish the time shape of the cure cycles. The variations of the processing window changed the rheological behavior of the resin during the cycle and promoting modifications in the microstructure of the composite material as well as the mechanical properties. The proposed cure cycles are showed in Figure 1 corresponding to an applied pressure of 2 bars.

In cycle C-1, the first hold at constant temperature has been removed in order to compare the effect of the omission in the process window. In cycles C-2 and C-3, a first hold has been fixed at 130ºC during 10minutes, but in the cycle C-3 a previous pick until 180ºC of heating has been introduced to expand the obtained process window. In all cycles, the gelification don’t take place until the second hold of the temperature profile is reached to guarantee that the values of viscosity, during the early stages of the cycle, are low enough to remove the voids located in the matrix. The process window is increased, by design, cycle to cycle.

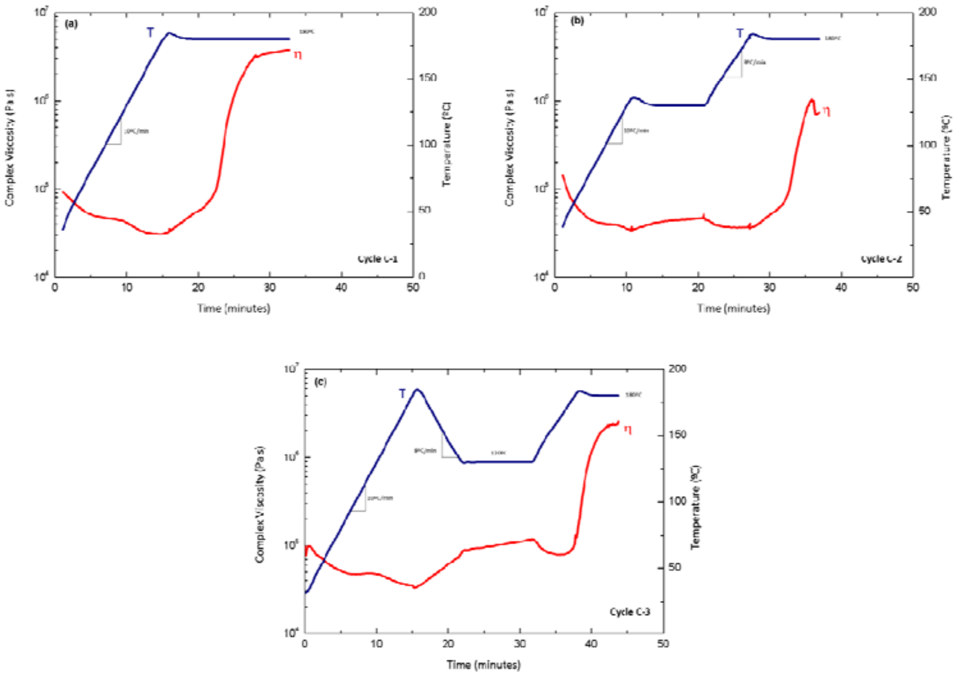


**Figure 1.** Temperature cure cycles used to process AS4/8552 composite prepreg and the corresponding evolution of the complex viscosity, η*, during the cycle, (a) cycle C-1; , (b) cycle C-2; , (c) cycle C-3;

Unidirectional, $[0°]_{10s}$, and multiaxial, $[45/0/-45/90]_{3S}$ and $[45_3/0_3/-45_3/90_3]_S$, laminates of an AS4/8552 polymer matrix composite were manufactured by compression molding under 2 bars of pressure and different temperature cycles. Similar degree of curing and glass transition temperature was achieved for all the cycles (Table 1).

| *Cycle* | *α* | $T_g$*(°C)* |
|---|---|---|
| C-1 | 0.891 | 207.6 |
| C-2 | 0.895 | 210.4 |
| C-3 | 0.896 | 210.6 |

**Table 1.** Degree of cure, *α*, and glass transition temperature, $T_g$, of AS4/8552 composite panels manufactured with different curing cycles.

## 4 Results and discussion

### *4.1 Volume fraction, shape and distribution of voids*

X-Ray computer tomography (CT) was used to ascertain the changes in the microstructure of the material due to the application of different cure cycles. Quantitative values of volumetric porosity, distribution, orientation and geometry of voids have been determined by computational treatment of the raw data obtained from CT scanning with 11-10 µm/voxel resolution. A binarized volume was used to fit each individual void to an equivalent cylinder of elliptical section whose volume, centroid and moments of inertia were equal to those of the void; Figure 2b shows the voxel reconstruction of a typical void and the corresponding equivalent cylinder.

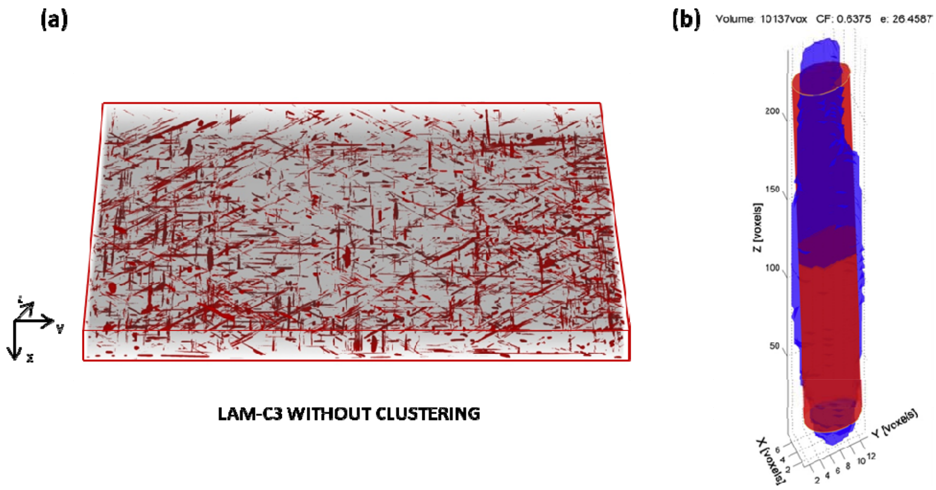


**Figure 2.** (a) X-ray microtomography of void spatial distribution in the quasi-isotropic composite panel manufactured following the staking sequence and according to the curing cycle C-3. (b) Typical rod-like void together with its equivalent cylinder.

XCT was used to obtain information about the void spatial distribution and shape within the panels. Voids were elongated and the elongation factor (length/average diameter) increased with void size. Most of the voids were the result of air entrapment and wrinkles created during lay-up. Voids were oriented parallel to the fibers as shown in Figure 2a in which carbon fibers and resins were set to semi-transparency to reveal the voids.

Images obtained by integrating the gray values of parallel slices along the fiber axis showed a cellular structure (figure 3). The cell walls were fiber-rich regions and porosity was localized at the center of the resin-rich cells. This peculiar distribution of the porosity within the laminate was the result of inhomogeneous consolidation. Low values of porosity were reached in case of multiaxial laminates respect to the unidirectional ones due to the lower packaging of fibers on these laminates.

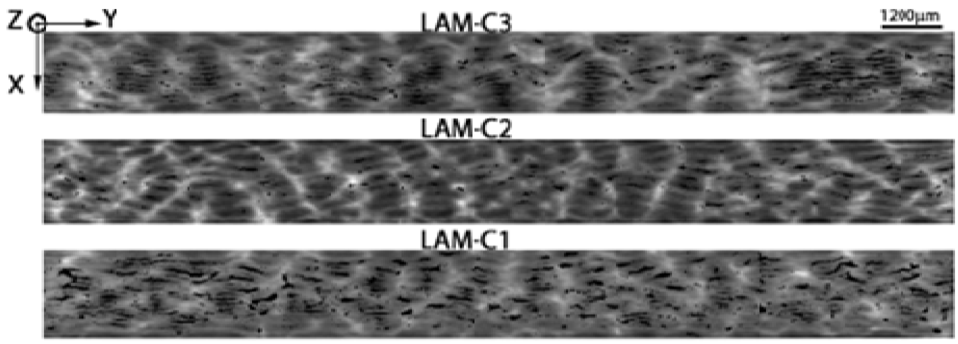


**Figure 3.** Average X-ray absorption of unidirectional composite panels along the fiber (Z-axis). Black zones stand for low density sections (pores), while white zones represent high density sections (fibers). Gray zones stand for matrix-rich regions.

The volume fraction of voids, Vf, was obtained directly from the tomograms by numerical integration of the individual volume of all the voids, and it is reported in Table X. Low values of porosity were reached in case of multiaxial laminates respect to the unidirectional ones due to the lower packaging in the multiaxial laminates.

*4.2 Mechanical properties*

Additionally, mechanical tests were performed on specimens machined from the composite panels manufactured with the different cure cycles in order to ascertain the effect of the processing voids on the mechanical performance of the composite material. In the case of unidirectional laminates: interlaminar shear strength (ILSS) and interlaminar fracture toughness, $G_{Ic}$ and $G_{IIc}$, were measured; for multiaxial laminates: in-plane compression strength, drop-weight impact and compressive residual strength (CAI) were measured.

The interlaminar strength values depend on the porosity level leads from the curing cycle used. The lower values of ILSS were obtained for those laminates in which the volumetric porosity was higher. The experimental values of interlaminar toughness in mode II also vary with the cure cycle used while in the case of mode I loading remain almost constant.

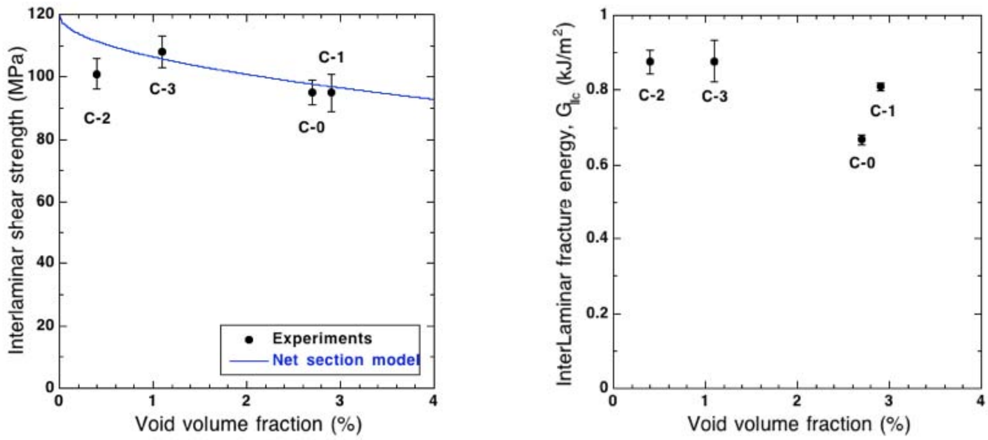


**Figure 4.** (a) ILSS strength of the AS4/8552 composite laminates as a function of void content. (b) Interlaminar fracture thoughness $G_{IIc}$ of composite laminates versus void content

The drop-weight impact and compressive residual strength of multiaxial laminates without and with clustering depend on layer clustering; however, no effects are measured as result of differences in their porosity levels. The compressive plain strength also depends on the curing cycle used, but this variation is higher in the case of multiaxial laminates without clustering.

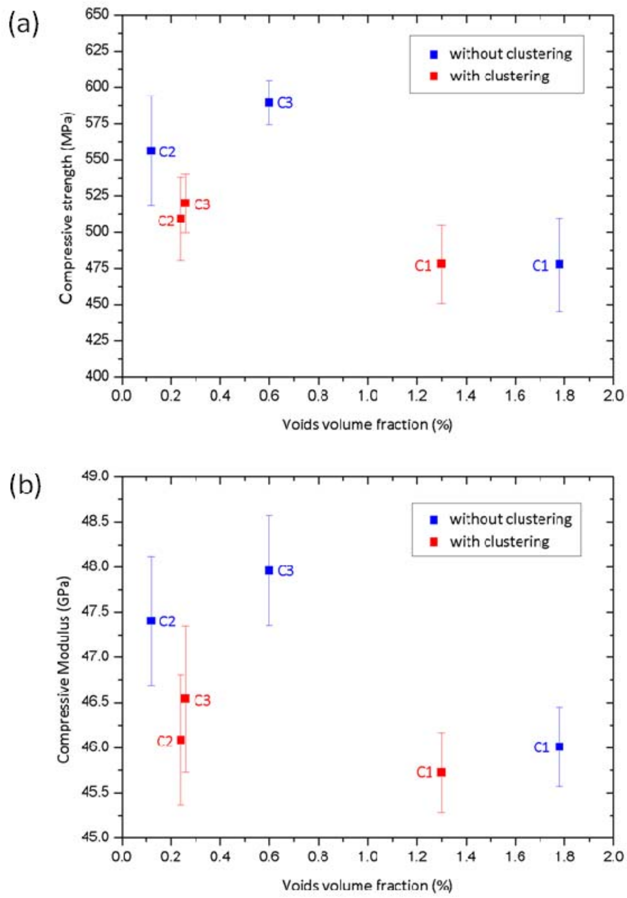


**Figure 6.** (a) Compression strength of the AS4/8552 composite laminates as a function of void content. (b) Compression modulus of composite laminates versus void content

# Conclusions

Unidirectional laminates of an AS4/8552 polymer matrix composite were manufactured by compression molding under 2 bars of pressure and different temperature cycles, which were designed according to the rheological and thermo-chemical behavior of the raw prepregs. Similar degree of curing and glass transition temperature was achieved for all the cycles. Longer processing windows (more time before gelation) led to laminates with lower fraction of voids for simple temperature cycles (involving only ramps and holds). In the case of complex cycles, involving flash temperatures followed by holds at lower temperatures, the final void volume fraction also depended on the actual evolution of the dynamic viscosity throughout the cycle. Low values of porosity were reached in case of multiaxial laminates respect to the unidirectional ones due to the lower packaging in the multiaxial laminates.

Void shape and spatial distribution was analyzed in detail by means of X-ray microtomography. Voids were elongated and the elongation factor (length/average diameter) increased with void size. Most of the voids were the result of air entrapment and wrinkles created during lay-up. They were oriented parallel to the fibers and concentrated in channels along the width of the laminate.

## References

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